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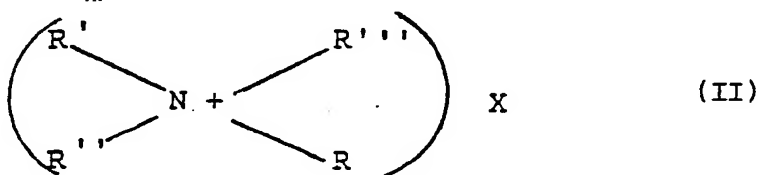
(54) Title: SYNTHESIS OF A CRYSTALLINE MOLECULAR SIEVE

Interplanar d-Spacings (A)

16.4 ± 0.2  
 8.2 ± 0.1  
 4.74 ± 0.05

Relative Intensity

VS  
 W  
 W (I)



## (57) Abstract

A method for synthesizing a large pore crystalline molecular sieve having an X-ray diffraction pattern with the characteristic lines (I), comprises (i) preparing a mixture comprising sources of oxides of aluminum, phosphorus, and optionally one or more elements (M) other than aluminum or phosphorus, water and a directing agent (DA), and having a composition, in terms of mole ratios, within the following ranges:  $M/Al_2O_3$ : 0 to 0.5,  $P_2O_5/Al_2O_3$ : 0.5 to 1.25,  $H_2O/Al_2O_3$ : 10 to 100,  $DA/Al_2O_3$ : 0.5 to 1.5 wherein DA is a compound of formula (II), wherein R, R', R'' and R''' are the same or different and are selected from  $-CH_2X$ ,  $-CH_2CH_2X$ , and X is a cation, (ii) maintaining said mixture under conditions including a temperature of 100°C to 145°C for a period of time of upto 80 hours and (iii) recovering the crystalline product from step (ii).

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SYNTHESIS OF A CRYSTALLINE MOLECULAR SIEVE

This invention relates to a method for synthesizing a crystalline molecular sieve having pore windows measuring greater than 10 Angstroms in diameter, such as, for example, greater than 12 Angstroms in diameter.

5           Zeolitic materials, both natural and synthetic, have been demonstrated in the past to have catalytic properties for various types of hydrocarbon conversion. Certain zeolitic materials are ordered, porous crystalline aluminosilicates having a definite crystalline structure as determined by X-ray diffraction, within  
10       which there are cavities which may be interconnected by channels or pores. These cavities and pores are uniform in size within a specific zeolitic material. Since the dimensions of these pores are such as to accept for adsorption molecules of certain dimensions while rejecting those of larger dimensions, these materials have  
15       come to be known as "molecular sieves" and are utilized in a variety of ways to take advantage of these properties.

      Such molecular sieves, both natural and synthetic, include a wide variety of positive ion-containing crystalline aluminosilicates. These aluminosilicates can be described as rigid  
20       three-dimensional frameworks of  $\text{SiO}_4$  and  $\text{AlO}_4$  in which the tetrahedra are cross-linked by the sharing of oxygen atoms whereby the ratio of the total aluminum and silicon atoms to oxygen atoms is 1:2. The electrovalence of the tetrahedra containing aluminum is balanced by the inclusion in the crystal of a cation, for example an  
25       alkali metal or an alkaline earth metal cation. This can be expressed wherein the ratio of aluminum to the number of various cations, such as  $\text{Ca}/2$ ,  $\text{Sr}/2$ , Na, K or Li, is equal to unity. One type of cation may be exchanged either entirely or partially with another type of cation utilizing ion exchange techniques in a  
30       conventional manner. By means of such cation exchange, it is possible to vary the properties of a given aluminosilicate by suitable selection of the cation.

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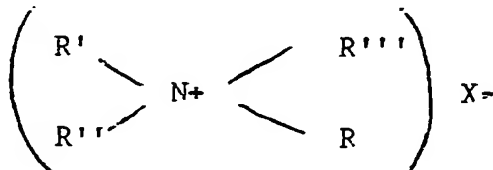
Prior art techniques have resulted in the formation of a great variety of synthetic zeolites. The zeolites have come to be designated by letter or other convenient symbols, as illustrated by zeolite A (U.S. Patent 2,882,243), zeolite X (U.S. Patent 2,882,244), zeolite Y (U.S. Patent 3,130,007), zeolite ZK-5 (U.S. Patent 3,247,195), zeolite ZK-4 (U.S. Patent 3,314,752), zeolite ZSM-5 (U.S. Patent 3,702,886), zeolite ZSM-11 (U.S. Patent 3,709,979), zeolite ZSM-12 (U.S. Patent 3,832,449), zeolite ZSM-20 (U.S. Patent 3,972,983), zeolite ZSM-35 (U.S. Patent 4,016,245), zeolite ZSM-38 (U.S. Patent 4,046,859), and zeolite ZSM-23 (U.S. Patent 4,076,842).

Porous aluminophosphates and their synthesis with the aid of organic directing agents are disclosed in U.S. Patent Nos. 4,310,440 and 4,385,994, whereas the synthesis of silicophosphoaluminates of various structures are disclosed in U.S. Patents 4,440,871 and 4,673,559. Methods for synthesizing crystalline metalloaluminophosphates are described in U.S. Patent No. 4,713,227.

The present invention resides in a method for synthesizing a crystalline molecular sieve having an X-ray diffraction pattern with lines shown in Table 1A of the specification, which comprises (i) preparing a mixture comprising sources of oxides of aluminum, phosphorus, and optionally one or more elements (M) other than aluminum or phosphorus, water and a directing agent (DA), and having a composition, in terms of mole ratios, within the following ranges:

M/Al <sub>2</sub> O <sub>3</sub>	0 to 0.5
P <sub>2</sub> O <sub>5</sub> /Al <sub>2</sub> O <sub>3</sub>	0.5 to 1.25
H <sub>2</sub> O/Al <sub>2</sub> O <sub>3</sub>	10 to 100
DA/Al <sub>2</sub> O <sub>3</sub>	0.5 to 1.5

wherein DA is a compound of the formula:



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wherein R, R'', R''' are the same or different and are selected from  $-CH_3X$  and  $-CH_2CH_2X$ , and X is a cation, (ii) maintaining said mixture under conditions including a temperature of 100°C to 145°C for a period of time of up to 80 hours and (iii) recovering the crystalline product from step (ii).

The crystalline molecular sieve produced according to the method of the invention has a framework topology which exhibits, even after being heated at 110°C or higher, a characteristic X-ray diffraction pattern having the following lines:

Table 1A

<u>Interplanar d-Spacings (A)</u>	<u>Relative Intensity</u>
16.4 $\pm$ 0.2	vs
8.2 $\pm$ 0.1	w
4.74 $\pm$ 0.05	w

and more specifically the following characteristic values:

Table 1B

<u>Interplanar d-Spacings (A)</u>	<u>Relative Intensity</u>
16.4 $\pm$ 0.2	vs
8.2 $\pm$ 0.1	w
$\left\{ \begin{array}{l} 6.21 \\ 6.17 \end{array} \right\} \pm 0.05$	w
5.48 $\pm$ 0.05	w
4.74 $\pm$ 0.05	w

and even more specifically the following characteristic values:

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Table 1C

	Interplanar d-Spacings (A)	Relative Intensity
	16.4 $\pm$ 0.2	vs
	8.2 $\pm$ 0.1	w
	(6.21) $\pm$ 0.05	w
5	(6.17) $\pm$ 0.05	w
	5.48 $\pm$ 0.05	w
	4.74 $\pm$ 0.05	w
	4.10 $\pm$ 0.04	w
	4.05 $\pm$ 0.04	w
	(3.96) $\pm$ 0.04	w
	(3.94) $\pm$ 0.04	w
10	3.76 $\pm$ 0.03	w
	3.28 $\pm$ 0.03	w

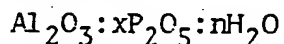
The X-ray diffraction lines in Tables 1A, 1B and 1C identify a crystal framework topology in the composition exhibiting large pore windows of 18-membered ring size. The pores are at least 10 Angstroms in diameter, such as for example at least 12 Angstroms, e.g. 12-13 Angstroms, in diameter. These lines distinguish this topology from other crystalline aluminosilicate, aluminophosphate and silicoaluminophosphate structures. It is noted that the X-ray pattern of the present composition is void of a d-spacing value at 13.6-13.3 Angstroms with any significant intensity relative the strongest d-spacing value. If a d-spacing value in this range appears in a sample of the present composition, it is due to impurity and will have a weak relative intensity.

These X-ray diffraction data were collected with conventional X-ray systems, using copper K-alpha radiation. The positions of the peaks, expressed in degrees 2 theta, where theta is the Bragg angle, were determined by scanning 2 theta. The interplanar spacings, d, measured in Angstrom units (A), and the relative intensities of the lines,  $I/I_0$ , where  $I_0$  is one-hundredth of the intensity of the strongest line, including subtraction of the background, were derived. The relative intensities are given in terms of the symbols vs = very strong (75-100%), s = strong (50-74%), m = medium (25-49%) and w = weak (0-24%). It should be understood that this X-ray diffraction

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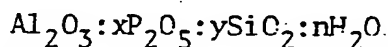
pattern is characteristic of all the species of the present compositions. Ion exchange of cations with other ions results in a composition which reveals substantially the same X-ray diffraction pattern with some minor shifts in interplanar spacing and variation in relative intensity. Relative intensity of individual lines may also vary relative the strongest line when the composition is chemically treated, such as by dilute acid treatment. Other variations can occur, depending on the composition component ratios of the particular sample, as well as its degree of thermal treatment. The relative intensities of the lines are also susceptible to changes by factors such as sorption of water, hydrocarbons or other components in the channel structure. Further, the optics of the X-ray diffraction equipment can have significant effects on intensity, particularly in the low angle region. Intensities may also be affected by preferred crystallite orientation.

More specifically, the molecular sieve produced by the method of the invention comprises a three-dimensional framework structure composed of tetrahedral units of  $AlO_2$ ,  $PO_2$  and optionally  $MO_2$ , where M is at least one element other than aluminum or phosphorus. Where the element M is absent, the molecular sieve has the following composition, in terms of mole ratios of oxides:



where x is 0.5 to 1.5, and n is 0-100 and preferably 0-10.

Where present, M is preferably silicon alone, in which case the molecular sieve has the following composition in terms of mole ratios of oxides:

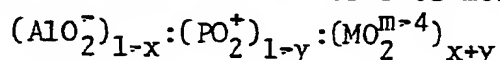


where x is 0.5 to 1.5, y is 0.01 to 0.5 and n is 0-100 and preferably 0-10.

Alternatively M includes an element other than silicon, such that the sum of the aluminum and phosphorus exceeds the number

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of M atoms and the molecular sieve has the following composition, in the anhydrous state and in terms of mole ratios of oxides:



together with anions and/or cations necessary for electrical neutrality and where m is the valence (or weighted average valence) of M, x and y satisfy the following relationship:

$$z = y - x + (4 + m) \cdot (x + y)$$

and z is greater than -1 and less than +1. When z is greater than 0, the molecular sieve will behave as a cation exchange material with potential use as an acidic catalyst. When z is less than 0, the molecular sieve will behave as an anion exchange material with potential use as a basic catalyst. In some cases silicon may also be present such that the ratio of silicon:non-silicon atoms is less than 1, preferably less than 0.5.

The element M in this alternative embodiment has an oxidation number of from +2 to +6, and an ionic "Radius Ratio" of 0.15 to 0.73, except that when the oxidation number of M is +2, the Radius Ratio of the element M is 0.52 to 0.62.

The term "Radius Ratio" is defined as the ratio of the crystal ionic radius of the element M to the crystal ionic radius of the oxygen anion,  $\text{O}^{2-}$ .

$$\text{Radius Ratio} = \frac{\text{crystal ionic radius of the element M}}{\text{crystal ionic radius of } \text{O}^{2-}}$$

The crystal ionic radii of elements are listed in the CRC Handbook of Chemistry and Physics, 61st edition, CRC Press, Inc., 1980, pages F-216 and F-217. In determining the Radius Ratio, it is necessary to use crystal ionic radii of the M atom and oxygen anion ( $\text{O}^{2-}$ ) which have been measured by the same method.



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Examples of element M useful herein include:

	<u>M</u>	<u>Valence</u>	<u>Radius Ratio</u>
5	As	+3	0.44
	B	+3	0.17
	Bi	+3	0.73
	Co	+2	0.55
	Cu	+2	0.54
10	Fe	+2	0.56
	Fe	+3	0.48
	Ge	+2	0.55
	Ge	+4	0.40
	In	+3	0.61
	Mn	+2	0.61
	Sb	+3	0.57
	Sn	+4	0.54
	Ti	+3	0.58
	Ti	+4	0.52
15	V	+3	0.56
	V	+4	0.48
	V	+5	0.45
	Zn	+2	0.56

Examples of elements not included as M of the present invention include:

	<u>Element</u>	<u>Valence</u>	<u>Radius Ratio</u>
20	B	+1	0.26
	Ba	+1	1.16
	Pa	+2	1.02
	Ce	+3	0.78
	Cd	+1	0.86
	Cd	+2	0.73
25	Cr	+1	0.61
	Cr	+2	0.67
	Cu	+1	0.73
	La	+1	1.05
	Mg	+1	0.62
	Mg	+2	0.50
	Mo	+1	0.70
	Sn	+2	0.70
	Sr	+2	0.85
	Th	+4	0.77
30	Ti	+1	0.73
	Ti	+2	0.71
	Zn	+1	0.67

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As synthesized, the crystalline composition will generally comprise structural aluminum, phosphorus and element M, and will exhibit an M/(aluminum plus phosphorus) atomic ratio of less than unity and greater than zero, and usually within the range of from 0.001 to 0.99. The phosphorus/aluminum atomic ratio of such materials may be found to vary from 0.01 to 100.0, as synthesized. It is well recognized that aluminum phosphates exhibit a phosphorus/aluminum atomic ratio of about unity, and essentially no element M. Also, the phosphorus-substituted zeolite compositions, sometimes referred to as "aluminosilicophosphate" zeolites, have a silicon/aluminum atomic ratio of usually greater than unity, and generally from 0.66 to 8.0, and a phosphorus/aluminum atomic ratio of less than unity, and usually from 0 to 1.

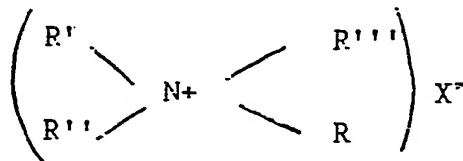
According to the invention, the molecular sieve described above is synthesized from a reaction mixture hydrogel containing sources of aluminum, phosphorus and optionally the non-aluminum, non-phosphorus element M, an organic directing agent, and water and having a composition, in terms of mole ratios, within the following ranges:

	<u>Broad</u>	<u>Preferred</u>	<u>Most Preferred</u>
$P_2O_5/Al_2O_3$	0.5 to 1.25	0.9 to 1.1	0.9 to 1.1
$H_2O/Al_2O_3$	10 to 100	20 to 80	30 to 60
$DA/Al_2O_3$	0.2 to 0.8	0.3 to 0.7	0.4 to 0.6

and when the element M is present:

$\tilde{M}/Al_2O_3$	0.01 to 0.5	0.01 to 0.2	0.01 to 0.1
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The directing agent DA is a compound represented by the formula:



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wherein R, R', R'' and R''' are the same as different and are selected from  $-\text{CH}_3\text{X}$  and  $-\text{CH}_2\text{CH}_2\text{X}$ , and X is a cation such as hydroxide or halide (e.g. chloride or bromide). Preferred examples of these compounds include tetrakis (2-hydroxyethyl) ammonium hydroxide, tetrakis (2-chloroethyl) ammonium chloride and tetrakis(hydroxymethyl) ammonium bromide.

Reaction conditions involve heating the foregoing reaction mixture to a temperature of 100°C to 145°C for 1 hour to 80 hours. A more preferred temperature range is from 130°C to 145°C with the amount of time at temperature being from 10 hours to 30 hours. If the temperature is higher than 145°C and/or the time exceeds 80 hours, the product composition will contain less of the desired large pore crystals characterized by the X-ray diffraction patterns of Tables 1A, 1B and 1C. Also important in the synthesis procedure is the ratio of  $\text{P}_2\text{O}_5/\text{Al}_2\text{O}_3$  in the reaction mixture. When the ratio  $\text{P}_2\text{O}_5/\text{Al}_2\text{O}_3$  is greater than about 1.25, especially if the temperature is higher than 145°C, product composition will contain decreased amounts of the desired crystalline material.

The solid product composition comprising the desired molecular sieve is recovered from the reaction medium, such as by cooling the whole to room temperature, filtering and water washing. The organic directing agent can then be removed from the product by conventional calcination procedures.

The synthesis method of the present invention is facilitated by the presence of seed crystals, such as those having the structure of the product crystals, in the reaction mixture. The use of at least 0.01%, preferably 0.10%, and even more preferably 1% seed crystals (based on total weight) of crystalline material in the reaction mixture will facilitate crystallization in the present method.

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The reaction mixture composition for the present method is prepared utilizing materials which supply the appropriate oxide. Useful sources of aluminum oxide include, as non-limiting examples, any known form of aluminum oxide or hydroxide, organic or inorganic salt or compound, e.g. alumina and aluminates. Such sources of aluminum oxide include pseudo-boehmite and aluminum tetraalkoxide. Useful sources of phosphorus oxide include, as non-limiting examples, any known form of phosphorus acids or phosphorus oxides, phosphates and phosphites, and organic derivatives of phosphorus. Useful sources of element M include, as non-limiting examples, any known form of non-aluminum, non-phosphorus element, e.g. metal, its oxide or hydride or salt, alkoxy or other organic compound containing M.

It will be understood that each oxide component utilized in the reaction mixture can be supplied by one or more essential reactants and they can be mixed together in any order. For example, any oxide can be supplied by an aqueous solution. The reaction mixture can be prepared either batchwise or continuously. Crystal size and crystallization time for the product composition comprising the desired metalloaluminophosphate will vary with the exact nature of the reaction mixture employed within the above-described limitations.

While the molecular sieve of the present invention may be used as an absorbent or as a catalyst component in a wide variety of organic compound, e.g. hydrocarbon compound, conversion reactions, it is notably useful as a catalyst in the processes of cracking, hydrocracking, isomerization and reforming. Other conversion processes for which the present composition may be utilized as a catalyst component include, for example, dewaxing.

The crystalline molecular sieve prepared in accordance herewith can be used either in the as-synthesized form, the hydrogen form or another univalent or multivalent cationic form. It can also be used in intimate combination with a hydrogenating component such as tungsten, vanadium, molybdenum, rhenium, nickel, cobalt,

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chromium, manganese, or a noble metal such as platinum or palladium where a hydrogenation-dehydrogenation function is to be performed. Such components can be exchanged into the composition, impregnated therein or physically intimately admixed therewith. Such components  
5 can be impregnated in or on to the crystalline composition such as, for example, by, in the case of platinum, treating the material with a platinum metal-containing ion. Suitable platinum compounds for this purpose include chloroplatinic acid, platinous chloride and various compounds containing the platinum amine complex.  
10 Combinations of metals and methods for their introduction can also be used.

The present composition, when employed either as an adsorbent or as a catalyst in a hydrocarbon conversion process, should be dehydrated at least partially. This can be done by  
15 heating to a temperature in the range of from 65°C to 315°C in an inert atmosphere, such as air and nitrogen, and at atmospheric or subatmospheric pressures for between 1 and 48 hours. Dehydration can be performed at lower temperature merely by placing the zeolite in a vacuum, but a longer time is required to obtain a particular  
20 degree of dehydration. The thermal decomposition product of the newly synthesized composition can be prepared by heating same at a temperature of from 200°C to 550°C for from 1 hour to 48 hours.

As above mentioned, synthetic metalloaluminophosphate prepared in accordance herewith can have the original cations  
25 associated therewith replaced by a wide variety of other cations according to techniques well known in the art. Typical replacing cations include hydrogen, ammonium and metal cations including mixtures thereof. Of the replacing metallic cations, particular preference is given to cations of metals such as rare earths and  
30 metals from Groups IIA, IIIA, IVA, IB, IIB, IIIB, IVB, VIB AND VIII of the Periodic Table of Elements, especially Mn, Ca, Mg, Zn, Cd, Pd, Ni, Cu, Ti, Al, Sn, Fe and Co.

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A typical ion exchange technique would be to contact the synthetic material with a salt of the desired replacing cation or cations. Although a wide variety of salts can be employed, particular preference is given to chlorides, nitrates and sulfates.

5 When used as a catalyst, it may be desirable to incorporate the molecular sieve of the invention with another material resistant to the temperatures and other conditions employed in organic conversion processes. Such matrix materials include active and inactive materials and synthetic or naturally occurring zeolites as  
10 well as inorganic materials such as clays, silica and/or metal oxides, e.g. alumina. The latter may be either naturally occurring or in the form of gelatinous precipitates, sols or gels including mixtures of silica and metal oxides. Use of an active material in conjunction with the present molecular sieve, i.e. combined  
15 therewith, may enhance the conversion and/or selectivity of the catalyst in certain organic conversion processes. Inactive materials suitably serve as diluents to control the amount of conversion in a given process so that products can be obtained economically and orderly without employing other means for  
20 controlling the rate or reaction. Frequently, crystalline catalytic materials have been incorporated into naturally occurring clays, e.g. bentonite and kaolin. These materials, i.e. clays, oxides, etc., function, in part, as binders for the catalyst. It is desirable to provide a catalyst having good crush strength, because  
25 in a petroleum refinery the catalyst is often subjected to rough handling, which tends to break the catalyst down into powder-like materials which cause problems in processing.

30 Naturally occurring clays which can be composited with the present molecular sieve include the montmorillonite and kaolin families which include the subbentonites, and the kaolins commonly known as Dixie, McNamee, Georgia and Florida clays, or others in which the main mineral constituent is halloysite, kaolinite,

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dickite, nacrite or anauxite. Such clays can be used in the raw state as originally mined or initially subjected to calcination, acid treatment or chemical modification.

In addition to the foregoing materials, the crystals hereby synthesized can be composited with a porous matrix material such as silica-alumina, silica-magnesia, silica-zirconia, silica-thoria, silica-beryllia, silica-titania, as well as ternary compositions such as silica-alumina-thoria, silica-alumina-zirconia, silica-alumina-magnesia and silica-magnesia-zirconia. The matrix can be in the form of a cogel. A mixture of these components could also be used.

The relative proportions of finely divided crystalline material and matrix vary widely with the crystalline material content ranging from 1 to 90 percent by weight, and more usually in the range of 2 to 50 percent by weight of the composite.

Employing a catalyst comprising the molecular sieve of this invention containing a hydrogenation component, reforming stocks can be reformed employing a temperature between 450°C and 550°C. The pressure can be between 445 and 3550 kPa (50 and 500 psig), but is preferably between 890 and 2170 kPa (100 and 300 psig). The liquid hourly space velocity is generally between 0.1 and 10 hr<sup>-1</sup>, preferably between 1 and 4 hr<sup>-1</sup> and the hydrogen to hydrocarbon mole ratio is generally between 1 and 10, preferably between 3 and 5.

A catalyst comprising the present composition can also be used for hydroisomerization of normal paraffins, when provided with a hydrogenation component, e.g. platinum. Hydroisomerization is carried out at a temperature between 250°C to 450°C, preferably 300°C to 425°C, with a liquid hourly space velocity between 0.1 and 10 hr<sup>-1</sup>, preferably between 0.5 and 4 hr<sup>-1</sup>, employing hydrogen such that the hydrogen to hydrocarbon mole ratio is between 1 and 10. Additionally, the catalyst can be used for olefin or aromatics isomerization employing temperatures between 0°C and 550°C.

A catalyst comprising the molecular sieve of this invention can also be used for reducing the pour point of gas oils. This

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process is carried out at a liquid hourly space velocity between 0.1 and 5 hr<sup>-1</sup> and a temperature between 300°C and 425°C.

This invention will now be more particularly described with reference to the Examples and the accompanying drawings in which  
5 Figures 1-8 are X-ray diffraction patterns of the calcined product of Examples 1 to 8 respectively.

#### Example 1

A mixture containing 103.5 g of 85% orthophosphoric acid  
10 (H<sub>3</sub>PO<sub>4</sub>) in 155 g water was mixed with 50.8 g aluminum oxide source (pseudo-boehmite). The mixture was heated to 80°C with stirring for 1 hour. To this mixture was added 105.5 g tetrakis(2-hydroxyethyl)ammonium hydroxide (DA) in 150 g water, giving a final reaction mixture composed as follows:

P <sub>2</sub> O <sub>5</sub> /Al <sub>2</sub> O <sub>3</sub>	=	1.26
H <sub>2</sub> O/Al <sub>2</sub> O <sub>3</sub>	=	52
DA/Al <sub>2</sub> O <sub>3</sub>	=	0.7

The reaction mixture was placed in a 1000 cc autoclave. Crystallization in the autoclave was at 140°C under 2170 kPa (300  
20 psig) nitrogen for 16 hours. The solid product was filtered, washed and dried. Washing was accomplished by extraction with water in a Soxhlet apparatus. The product was calcined at 538°C in air for 10 hours.

The calcined product was analyzed by X-ray powder  
25 diffraction and found to be crystalline and to show the pattern of Table 2 and Figure 1.



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Table 2

	<u>Interplanar d-Spacings (A)</u>	<u>Observed 2xTheta</u>	<u>Relative Intensities (I/I<sub>0</sub>)</u>
5	19.62633	4.502	2.0
	16.50637	5.354	100.0
	11.95308	7.396	7.1
	8.24634	10.728	27.2
	6.20381	14.277	12.9
10	4.74095	18.717	12.7
	4.33935	20.467	1.4
	4.19087	21.200	4.5
	4.08690	21.746	57.1
	4.06799	21.848	67.2
15	3.96914	22.399	42.0
	3.95098	22.504	46.0
	3.79405	23.447	13.3
	3.77009	23.598	24.3
	3.58563	24.831	5.7
20	3.50222	25.433	0.4
	3.47553	25.631	1.4
	3.43484	25.940	2.2
	3.41076	26.126	1.0
	3.28214	27.169	32.2
25	3.17008	28.149	4.9
	3.15501	28.287	4.4
	3.08670	28.926	14.2
	3.08117	28.979	11.1
	3.03351	29.445	2.3
30	2.95461	30.249	9.2
	2.95086	30.289	10.4
	2.91456	30.675	1.4
	2.81518	31.786	0.9
	2.73786	32.709	12.7
	2.73145	32.788	7.4

Chemical analysis of the extracted Example 1 product indicated the following composition:

30	Al	19.63 wt.%
	P	21.04 wt.%
	Si	0.026 wt.%
	Na	0.029 wt.%

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Example 2

A mixture containing 115 g of 85% orthophosphoric acid ( $\text{H}_3\text{PO}_4$ ) in 155 g water was mixed with 71 g aluminum oxide source (pseudo-boehmite). The mixture was heated to 80°C with stirring for 3 hours. To this mixture was added 105.5 g tetrakis(2-hydroxyethyl)ammonium hydroxide (DA) in 150 g water, giving a final reaction mixture composed as follows:

$\text{P}_2\text{O}_5/\text{Al}_2\text{O}_3$	=	1
$\text{H}_2\text{O}/\text{Al}_2\text{O}_3$	=	40
$\text{DA}/\text{Al}_2\text{O}_3$	=	0.5

The reaction mixture was placed in a 1000 cc autoclave. Crystallization in the autoclave was at 142°C under 2170 kPa (300 psig) nitrogen for 17 hours. The solid product was filtered, washed and dried. Washing was accomplished by extraction with water in a Soxhlet apparatus. The product was calcined at 530°C in air for 10 hours.

The calcined product was analyzed by X-ray powder diffraction and found to be crystalline and to show the pattern of Table 3 and Figure 2.

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The reaction mixture was placed in an autoclave. Crystallization in the autoclave was at 138°C under 2170 kPa (300 psig) nitrogen for 14 hours. The solid product was filtered, washed and dried. Washing was accomplished by extraction with water in a Soxhlet apparatus. The product was calcined at 530°C in air for 10 hours.

The calcined product was analyzed by X-ray powder diffraction and found to be crystalline and to show the pattern of Table 4 and Figure 3.

Table 3

	<u>Interplanar d-Spacings (A)</u>	<u>Observed 2xTheta</u>	<u>Relative Intensities (I/I<sub>0</sub>)</u>
15	16.57941}	5.330	75.6
	16.43716}	5.376	100.0
	8.21396	10.771	23.9
	6.16367	14.370	13.9
	4.73769	18.730	12.8
	4.09134}	21.722	45.6
	4.05906}	21.897	56.6
	3.96168}	22.442	30.8
20	3.93658}	22.587	34.6
	3.77338	23.578	18.3
	3.42679	26.002	1.9
	3.28000	27.188	30.3
	3.19718	27.906	1.1
	3.16223	28.221	5.3
	3.07912	28.999	12.3
25	2.95194	30.277	10.7
	2.94785	30.320	12.1
	2.89369	30.902	3.2
	2.73464	32.748	13.5
	2.58822	34.658	0.6

Chemical analysis of the extracted Example 2 product indicated the following composition:

Al	19.46 wt. %
P	16.63 wt. %
Si	0.046 wt. %
Na	0.033 wt. %

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Example 3

A mixture containing 57.5 g of 85% orthophosphoric acid ( $H_3PO_4$ ) in 77.5 g water was mixed with 35.5 g aluminum oxide source (pseudo-boehmite). The mixture was heated to 80°C with stirring for 1 hour. To this mixture was added 52.75 g tetrakis(2-hydroxyethyl)ammonium hydroxide (DA) in 75 g water, giving a final reaction mixture composed as follows:

$P_2O_5/Al_2O_3$	=	1
$H_2O/Al_2O_3$	=	41
$DA/Al_2O_3$	=	0.5

The reaction mixture was placed in an autoclave. Crystallization in the autoclave was at 138°C under 2170 kPa (300 psig) nitrogen for 14 hours. The solid product was filtered, washed and dried. Washing was accomplished by extraction with water in a Soxhlet apparatus. The product was calcined at 530°C in air for 10 hours.

The calcined product was analyzed by X-ray powder diffraction and found to be crystalline and to show the pattern of Table 4 and Figure 3.

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Table 4

	<u>Interplanar d-Spacings (Å)</u>	<u>Observed 2xTheta</u>	<u>Relative Intensities (I/I<sub>0</sub>)</u>
	16.33147	5.411	100.0
	8.19161	10.800	24.4
	6.15847	14.382	13.7
5	4.73260	18.750	13.5
	4.46994	19.863	1.1
	4.07984	21.784	54.7
	4.05933	21.895	61.4
	3.95056	22.506	38.3
	3.93839	22.576	39.4
	3.77224	23.585	16.9
	3.76217	23.649	23.5
10	3.62809	24.536	8.9
	3.58473	24.838	8.0
	3.27475	27.232	34.8
	3.16219	28.221	8.4
	3.07736	29.016	14.9
	3.02653	29.514	8.7
	2.94680	30.331	16.9
15	2.89666	30.869	8.4
	2.88632	30.983	9.2
	2.74261	32.650	11.0
	2.73319	32.766	12.4
	2.72987	32.807	9.7

Chemical analysis of the extracted Example 3 product  
 20 indicated the following composition:

Al	21.33 wt.%
P	20.13 wt.%
Si	0.028 wt.%
Na	0.021 wt.%

25 Example 4 (Comparative)

A mixture containing 61.5 g of 85% orthophosphoric acid  
 (H<sub>3</sub>PO<sub>4</sub>) in 92.1 g water was mixed with 30.2 g aluminum oxide  
 source (pseudo-boehmite). The mixture was heated to 80°C with  
 30 stirring for 1 hour. To this mixture was added 62.7 g  
 tetrakis(2-hydroxyethyl)ammonium hydroxide (DA) in 89.2 g water,  
 giving a final reaction mixture composed as follows:

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$P_2O_5/Al_2O_3$	=	1.28
$H_2O/Al_2O_3$	=	52
$DA/Al_2O_3$	=	0.71

The reaction mixture was placed in an autoclave. Crystallization in the autoclave was at 160°C under 2170 kPa (300 psig) nitrogen for 5 hours. The solid product was filtered, washed with water and dried.

The product was analyzed by X-ray powder diffraction and found to be crystalline and to show the pattern of Table 5 and Figure 4.

Table 5

	<u>Interplanar d-Spacings (Å)</u>	<u>Observed 2xTheta</u>	<u>Relative Intensities (I/I<sub>0</sub>)</u>
15	11.83947	7.467	56.4
	6.83277	12.957	9.2
	5.91531	14.977	23.9
	4.46975	19.863	57.5
	4.23470	20.978	47.9
	3.94108}	22.561	56.7
	3.95335}	22.490	100.0
20	3.59716	24.750	5.1
	3.41379	26.103	36.8
	3.30072	27.014	0.0
	3.07036}	29.083	13.3
	3.06515}	29.134	11.7
	2.95580	30.237	21.4
	2.65608	33.746	5.0
25	2.58051	34.765	17.1

The product of Example 4, crystallized from the indicated reaction mixture at 160°C was found to be primarily  $AlPO_4 \cdot 5H_2O$ , void of any significant amount of the large pore aluminophosphate crystals of the present synthesis invention.

Example 5

A mixture containing 56.4 g of 85% orthophosphoric acid ( $H_3PO_4$ ) in 77.5 g water was mixed with 35.5 g aluminum oxide source (e.g. pseudo-boehmite) and 0.6 g silicon oxide source (e.g.

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HiSi1). The mixture was heated to 80°C with stirring for 1 hour. To this mixture was added 52.75 g tetrakis(2-hydroxyethyl)ammonium hydroxide (DA) in 75 g water, giving a final reaction mixture composed as follows:

SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	=	0.04
P <sub>2</sub> O <sub>5</sub> /Al <sub>2</sub> O <sub>3</sub>	=	1
H <sub>2</sub> O/Al <sub>2</sub> O <sub>3</sub>	=	41
DA/Al <sub>2</sub> O <sub>3</sub>	=	0.5

The reaction mixture was placed in a 300 cc autoclave.

Crystallization in the autoclave was at 142°C under 2170 kPa (300 psig) nitrogen for 17 hours. The solid product was filtered, washed and dried. Washing was accomplished by extraction with water in a Soxhlet apparatus. The product was calcined at 530°C in air for 10 hours.

The calcined product was analyzed by X-ray powder diffraction and found to be crystalline and to show the pattern of Table 6 and Figure 5.

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Table 6

	<u>Interplanar d-Spacings (Å)</u>	<u>Observed 2xTheta</u>	<u>Relative Intensities (I/I<sub>0</sub>)</u>
	16.68787}	5.296	58.5
	16.26226}	5.434	100.0
	8.89212	9.947	7.3
5	8.17058	10.828	20.6
	6.13784	14.431	11.1
	5.46353	16.223	1.8
	4.73902}	18.724	9.0
	4.70722}	18.852	8.4
	4.07994}	21.783	67.3
	4.07134}	21.830	61.1
10	4.05055	21.943	53.7
	3.96029}	22.450	32.3
	3.94729}	22.525	38.9
	3.92603}	22.649	46.9
	3.75873	23.671	16.2
	3.62657	24.547	3.4
	3.33667	26.717	2.3
	3.31352	26.907	2.4
15	3.27994	27.188	21.1
	3.26921	27.279	23.0
	3.15504	28.286	3.8
	3.07718	29.018	8.4
	3.02872	29.492	2.4
	3.01346	29.645	1.2
	2.98113	29.974	0.4
20	2.95165	30.280	6.5
	2.94100	30.393	9.0
	2.82514	31.671	0.0
	2.75903	32.451	2.0

Chemical analysis of the extracted Example 5 product indicated the following composition:

25

Al	22.09 wt.%
P	18.84 wt.%
Si	0.29 wt.%
Na	0.04 wt.%



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Example 6 (Comparative)

A mixture containing 55.8 g of 85% orthophosphoric acid ( $\text{H}_3\text{PO}_4$ ) in 77.5 g water was mixed with 35.5 g aluminum oxide source (e.g. pseudo-boehmite) and 1.0 g silicon oxide source (e.g. HiSil). The mixture was heated to 80°C with stirring for 1 hour. To this mixture was added 52.75 g tetrakis(2-hydroxyethyl)ammonium hydroxide (DA) in 75 g water, giving a final reaction mixture composed as follows:

$\text{SiO}_2/\text{Al}_2\text{O}_3$	=	0.068
$\text{P}_2\text{O}_5/\text{Al}_2\text{O}_3$	=	1
$\text{H}_2\text{O}/\text{Al}_2\text{O}_3$	=	41
$\text{DA}/\text{Al}_2\text{O}_3$	=	0.5

The reaction mixture was placed in a 300 cc autoclave. Crystallization in the autoclave was at 151°C under 2170 kPa (300 psig) nitrogen for 20 hours. The solid product was filtered, washed with nitrogen for 16 hours. The solid product was filtered, washed and dried at 110°C for 17 hours.

The product was analyzed by X-ray powder diffraction and found to be crystalline and to show the pattern of Table 7 and Figure 6.

Table 7

<u>Interplanar</u> <u>d-Spacings (Å)</u>	<u>Observed</u> <u>2xTheta</u>	<u>Relative</u> <u>Intensities (I/I<sub>0</sub>)</u>
11.87357	7.445	56.6
6.84887	12.926	9.5
5.92402	14.955	26.1
4.47513	19.839	60.8
4.22879	21.008	57.8
3.95662	22.471	100.0
3.59569	24.761	4.9
3.41744	26.074	35.1
3.25865	27.369	0.5
3.07050	29.082	15.8
2.95952	30.198	19.3
2.65784	33.722	5.0
2.58301	34.730	15.4

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The product of Example 6, crystallized from the indicated reaction mixture at 151°C for 20 hours was primarily SAPO-5 and was void of any significant amount of the large pore silicoaluminophosphate crystals of the present synthesis invention.

#### Example 7

A mixture containing 56.6 g of 85% orthophosphoric acid ( $\text{H}_3\text{PO}_4$ ) in 77.5 g water was mixed with 0.46 g of vanadium pentoxide ( $\text{V}_2\text{O}_5$ ). The mixture was heated to 50°C with stirring for 30 minutes until complete dissolution of the vanadium pentoxide. Then, 35.5 g of aluminum oxide source (e.g. pseudo-boehmite) was added and the mixture was heated to 80°C for 1 hour. To this mixture was added 52.75 g tetrakis(2-hydroxyethyl)ammonium hydroxide (DA) in 75 g water, giving a final reaction mixture composed as follows:

M/ $\text{Al}_2\text{O}_3$	=	0.01
$\text{P}_2\text{O}_5/\text{Al}_2\text{O}_3$	=	1
$\text{H}_2\text{O}/\text{Al}_2\text{O}_3$	=	40
DA/ $\text{Al}_2\text{O}_3$	=	0.5

The reaction mixture was placed in a 300 cc autoclave. Crystallization in the autoclave was at 142°C at autogenous pressure for 17 hours. The solid product was filtered, washed and dried. Washing was accomplished by extraction with water in a Soxhlet apparatus. The product was calcined at 530°C in air for 10 hours.

The calcined product was analyzed by X-ray powder diffraction and found to be crystalline and to show the pattern of Table 8 and Figure 7.

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Table 8

	<u>Interplanar d-Spacings (A)</u>	<u>Observed 2xTheta</u>	<u>Relative Intensities (I/I<sub>0</sub>)</u>
	16.57872)	5.330	44.6
	16.35191}	5.404	53.7
5	14.10361	6.267	2.6
	8.24762	10.727	9.0
	6.16987	14.356	6.1
	5.70737	15.526	4.1
	5.49256	16.137	1.8
	5.13743	17.261	1.5
	4.83746	18.340	1.8
10	4.63375	19.154	0.5
	4.48486	19.796	7.2
	4.44217	19.988	3.4
	4.38940	20.231	0.2
	4.09681	21.693	100.0
	3.95979	22.453	44.6
	3.93834	22.577	56.9
	3.92046	22.681	38.3
15	3.55416	25.055	8.4
	3.52731	25.249	4.2
	3.45606	25.778	0.9
	3.43090	25.970	0.6
	3.40681	26.157	1.7
	3.32695	26.797	6.0
	3.28900	27.112	15.8
	3.26948	27.277	18.3
20	3.15962	28.244	0.8
	3.09672	28.830	4.9
	3.08958	28.898	6.3
	3.08135	28.977	7.0
	3.02691	29.510	9.7
	2.98840	29.899	5.1
	2.95680	30.226	1.5
25	2.94644	30.335	0.4
	2.90223	30.809	2.4
	2.82792	31.639	2.4
	2.77318	32.281	2.2
	2.73918	32.692	5.5
	2.72426	32.877	2.3
	2.67483	33.502	0.7
	2.60065	34.487	1.1
30	2.57558	34.833	0.3

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Chemical analysis of the extracted Example 7 product indicated the following composition:

Al	18.75 wt.%
P	17.39 wt.%
V	0.19 wt.%
Si	0.17 wt.%

Example 8 (Comparative)

A mixture containing 56.6 g of 85% orthophosphoric acid ( $H_3PO_4$ ) in 77.5 g water was mixed with 0.46 g of vanadium pentoxide ( $V_2O_5$ ). The mixture was heated to 50°C with stirring for 30 minutes until complete dissolution of the vanadium pentoxide. Then, 35.5 g of aluminum oxide source (e.g. pseudo-boehmite) was added and the mixture was heated to 80°C for 1 hour. To this mixture was added 52.75 g tetrakis(2-hydroxyethyl)ammonium hydroxide (DA) in 75 g water, giving a final reaction mixture composed as follows:

M/ $Al_2O_3$	=	0.01
$P_2O_5/Al_2O_3$	=	1
$H_2O/Al_2O_3$	=	40
DA/ $Al_2O_3$	=	0.5

The reaction mixture was placed in a 300 cc autoclave. Crystallization in the autoclave was at 147°C at autogenous pressure for 17 hours. The solid product was filtered, washed with water and dried at 110°C for 17 hours.

The product was analyzed by X-ray powder diffraction and found to be crystalline and to show the pattern of Table 9 and Figure 8.

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Table 9

	<u>Interplanar d-Spacings (A)</u>	<u>Observed 2xTheta</u>	<u>Relative Intensities (I/I<sub>0</sub>)</u>
	11.86314	7.452	56.5
	6.84404	12.935	10.0
5	5.92515	14.952	24.7
	4.47602	19.835	57.1
	4.20617	21.122	51.4
	3.95363	22.488	100.0
	3.58446	24.840	3.1
	3.41877	26.064	34.6
	3.19075	27.963	0.4
	3.06316	29.153	14.7
10	2.96016	30.191	17.9
	2.65390	33.774	4.4
	2.58432	34.712	13.7

15      The product of Example 8 was composed primarily of crystals having the structure of  $\text{AlPO}_4\text{-5}$ , with only a small amount of the large pore metalloaluminophosphate crystals of the present invention.

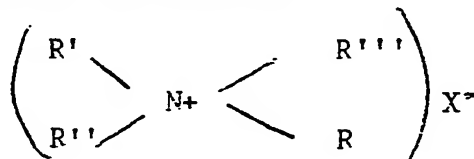
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CLAIMS:

1. A method for synthesizing a crystalline molecular sieve having an X-ray diffraction pattern with lines shown in Table 1A of the specification, which comprises (i) preparing a mixture comprising sources of oxides of aluminum, phosphorus, and optionally one or more elements (M) other than aluminum or phosphorus, water and a directing agent (DA), and having a composition, in terms of mole ratios, within the following ranges:

M/Al <sub>2</sub> O <sub>3</sub>	0 to 0.5
P <sub>2</sub> O <sub>5</sub> /Al <sub>2</sub> O <sub>3</sub>	0.5 to 1.25
H <sub>2</sub> O/Al <sub>2</sub> O <sub>3</sub>	10 to 100
DA/Al <sub>2</sub> O <sub>3</sub>	0.5 to 1.5

wherein DA is a compound of the formula:



wherein R, R', R'' and R''' are the same or different and are selected from -CH<sub>3</sub>X, -CH<sub>2</sub>CH<sub>2</sub>X, and X is a cation, (ii) maintaining said mixture under conditions including a temperature of 100°C to 145°C for a period of time of up to 80 hours and (iii) recovering the crystalline product from step (ii).

2. The method of claim 1 wherein M is present in the reaction mixture and M/Al<sub>2</sub>O<sub>3</sub> is 0.01 to 0.5.

3. The method of claim 1 wherein the mixture has the following composition ranges:

P <sub>2</sub> O <sub>5</sub> /Al <sub>2</sub> O <sub>3</sub>	0.9 to 1.1
H <sub>2</sub> O/Al <sub>2</sub> O <sub>3</sub>	20 to 80
DA/Al <sub>2</sub> O <sub>3</sub>	0.3 to 0.7

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4. The method of claim 3 wherein M is present in the reaction mixture and  $M/Al_2O_3$  is 0.01 to 0.2

5. The method of Claim 1 wherein said mixture has the following composition ranges:

$P_2O_5/Al_2O_3$	0.9 to 1.1
$H_2O/Al_2O_3$	30 to 60
$DA/Al_2O_3$	0.4 to 0.6

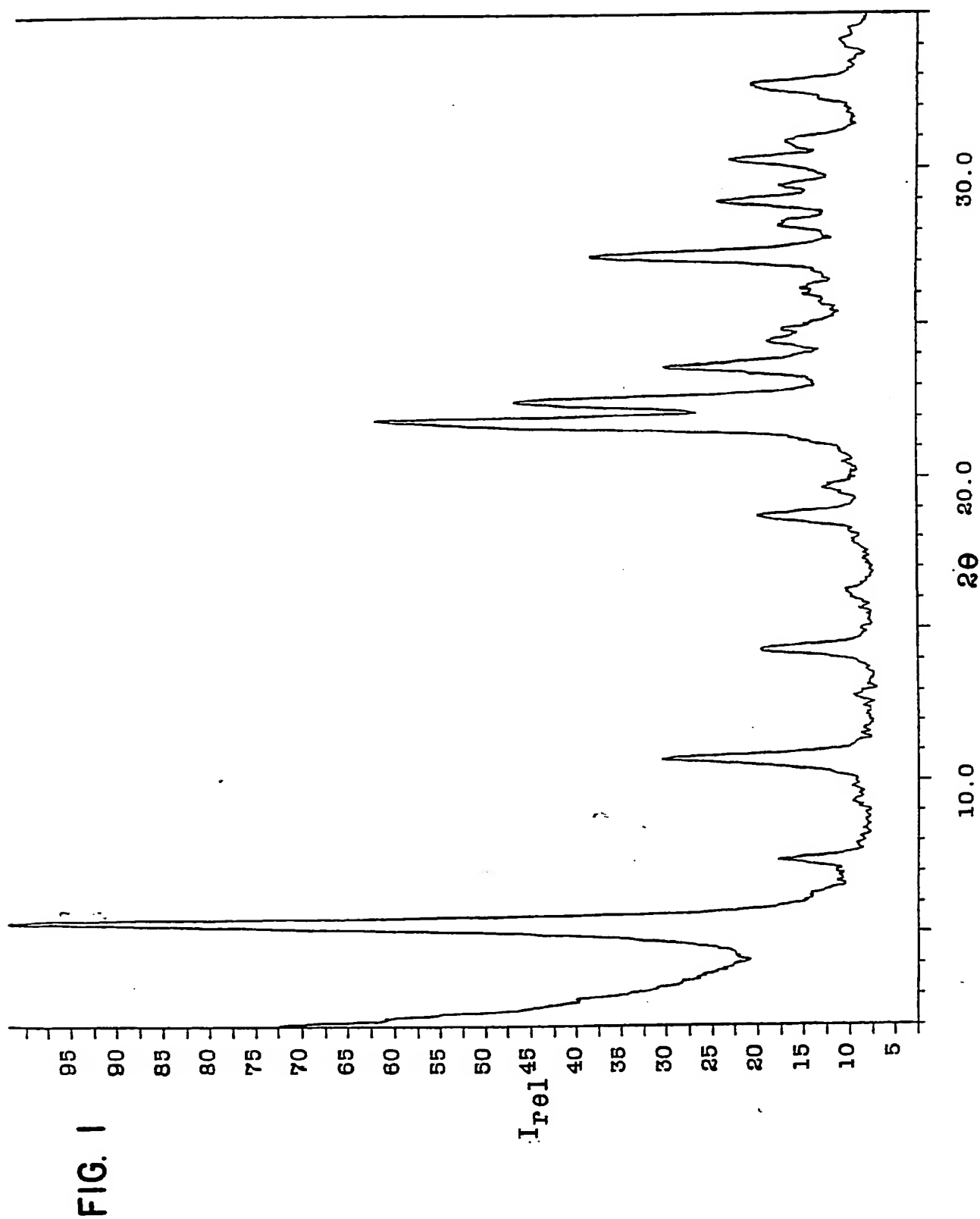
6. The method of claim 5 wherein M is present in the reaction mixture and  $M/Al_2O_3$  is 0.01 to 0.1

7. The method of claim 2 wherein M includes an element other than silicon having an oxidation number +2 and an ionic radius ratio of 0.52 to 0.62 or an oxidation number of +3 to +6 and an ionic radius ratio of 0.15 to 0.73.

8. The method of claim 2 wherein M includes  $In^{3+}$ ,  $Sb^{4+}$ ,  $Sn^{4+}$ ,  $Ti^{3+}$  or  $Ti^{4+}$ .

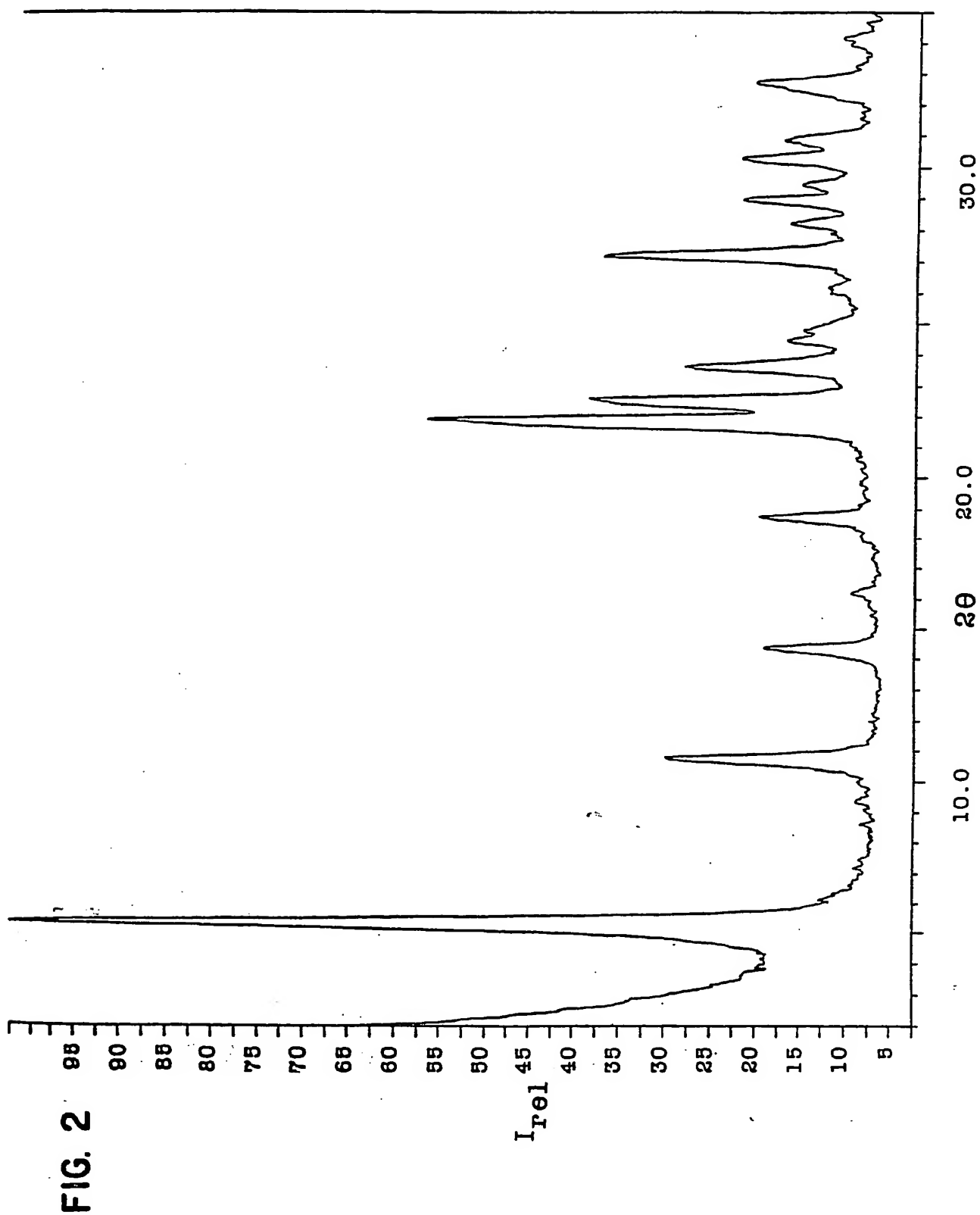
9. The method of claim 2, wherein M also includes silicon such that the ratio of silicon:non-silicon atoms in the  $MO_2$  component is less than 1.

10. The method of claim 1 wherein the directing agent DA is tetrakis(2-(hydroxyethyl)ammonium hydroxide).

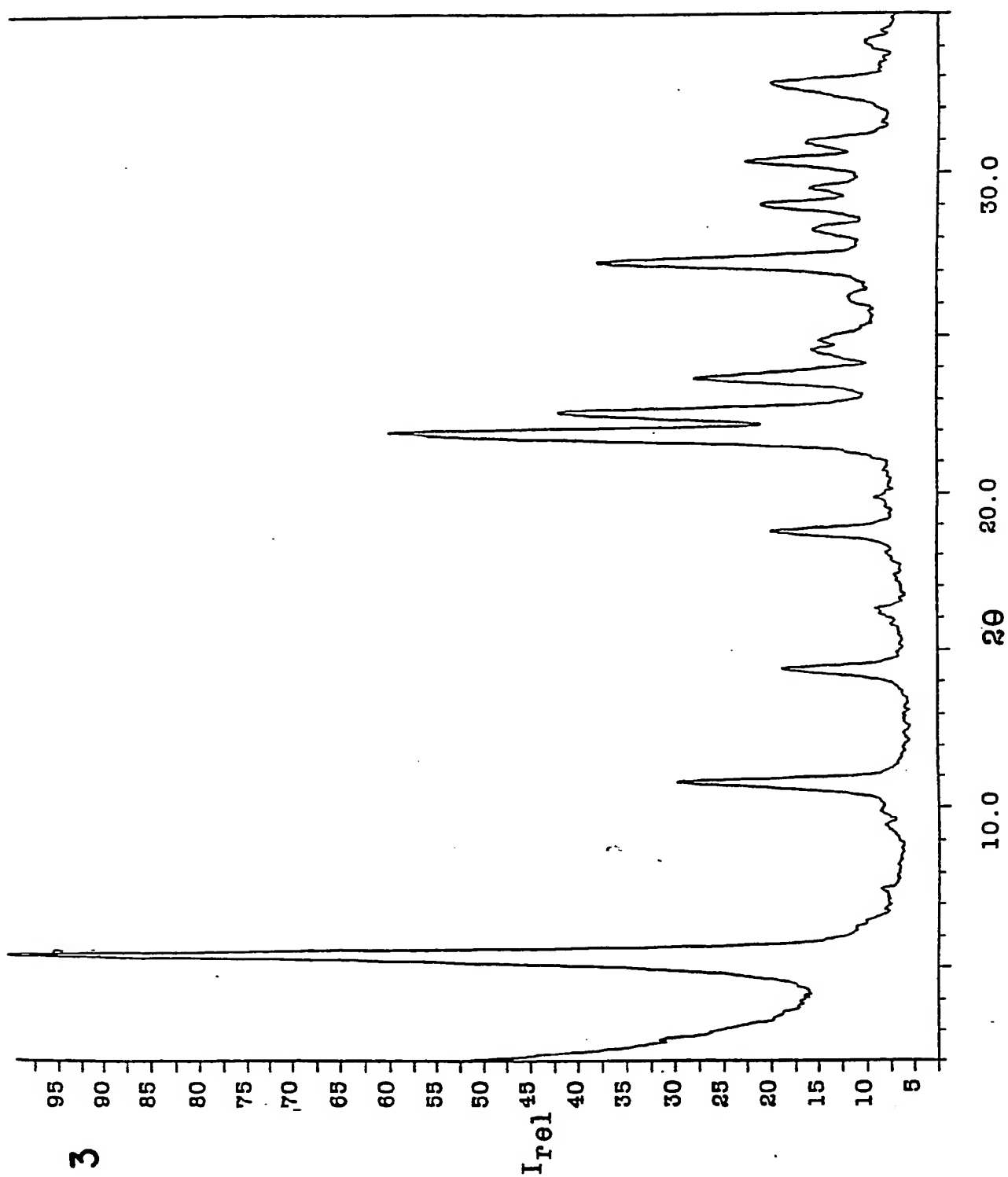




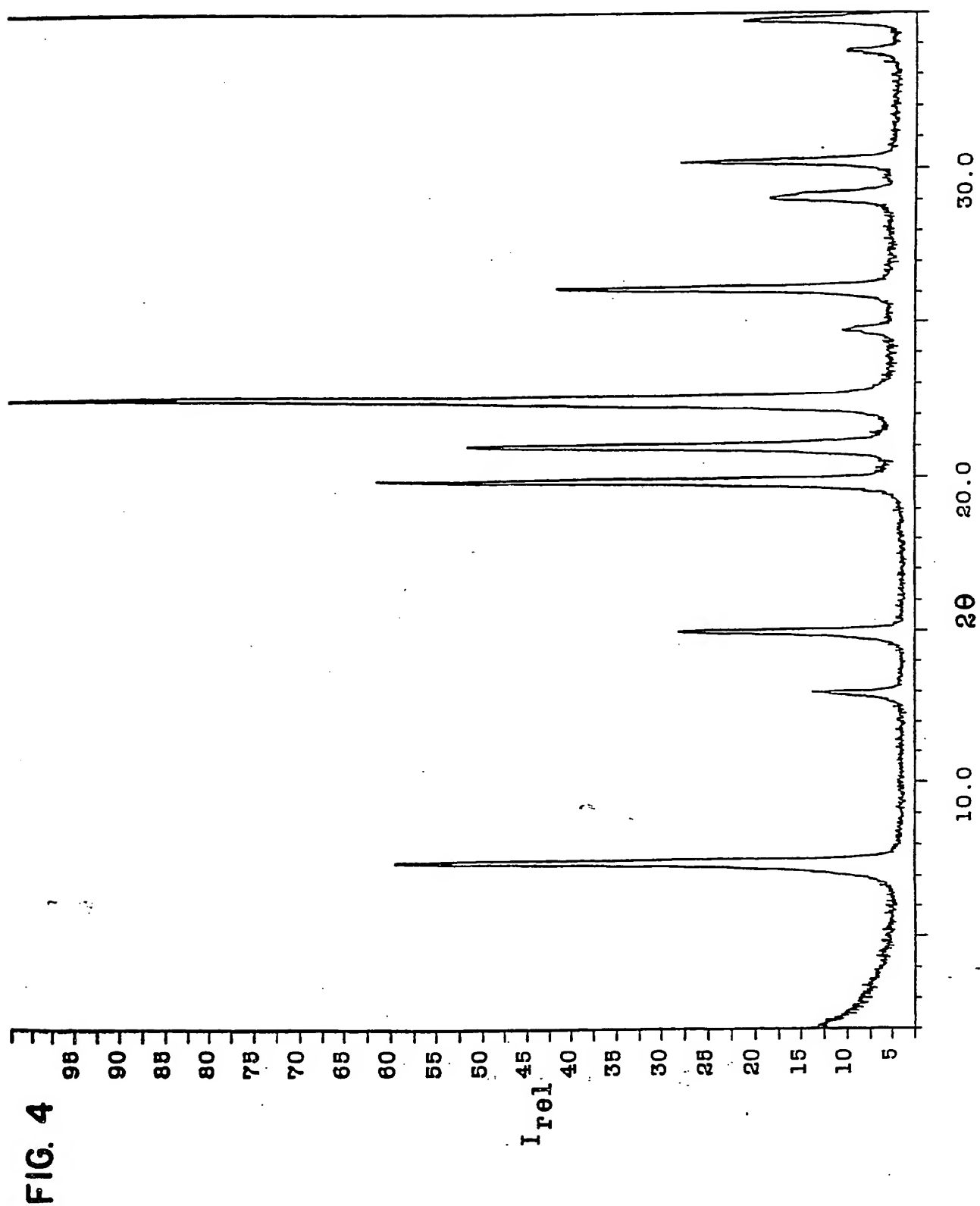
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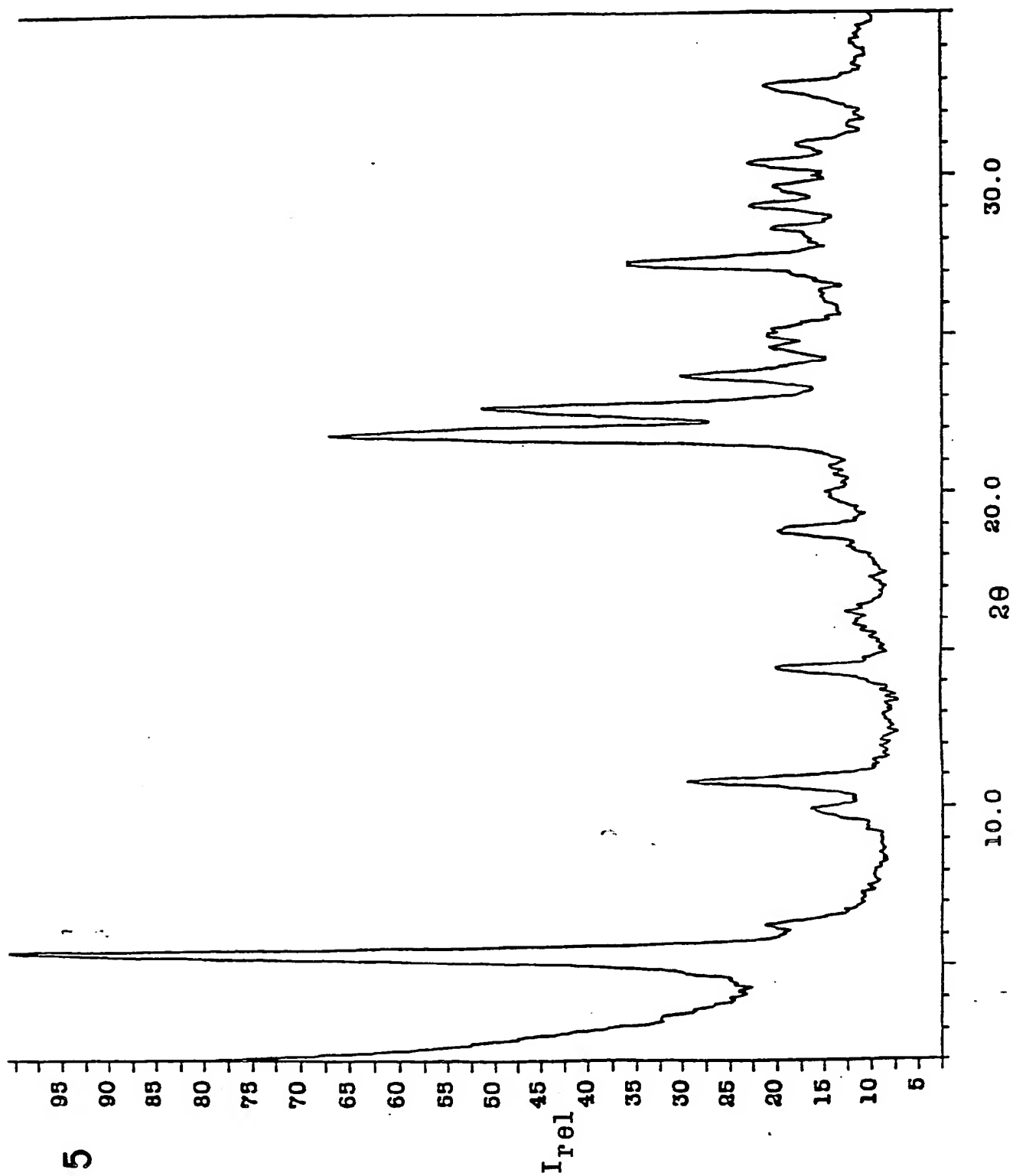
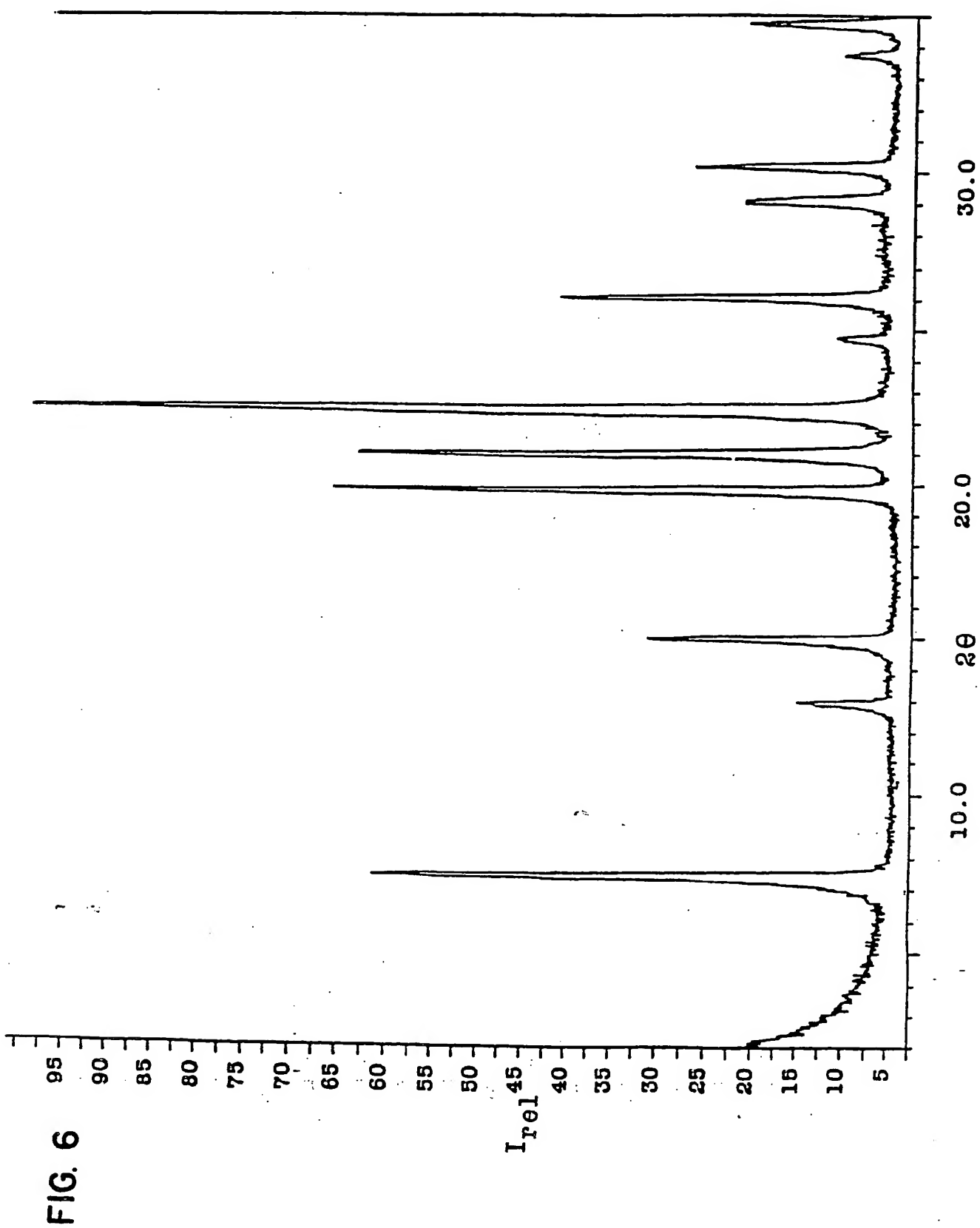


FIG. 5

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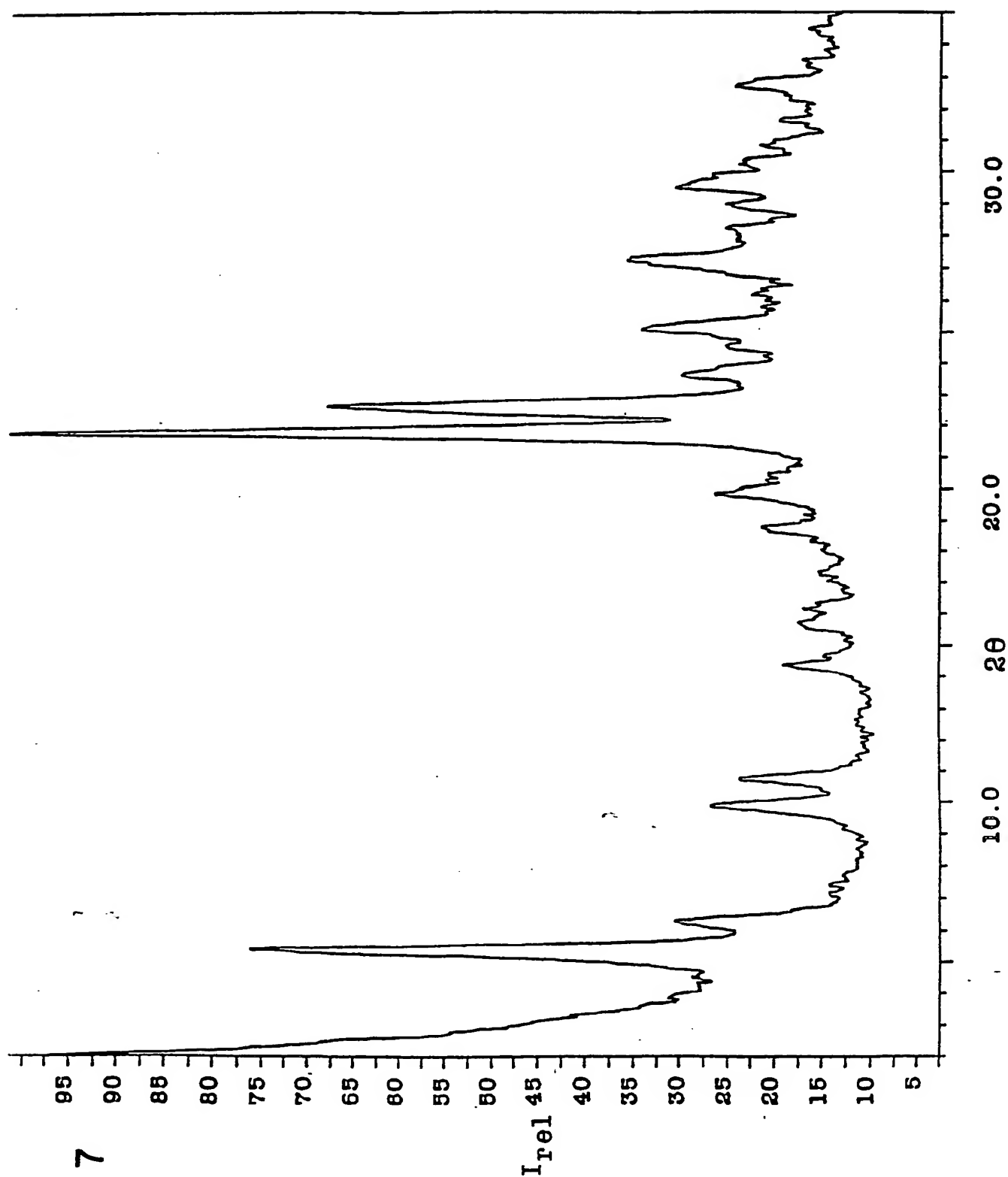
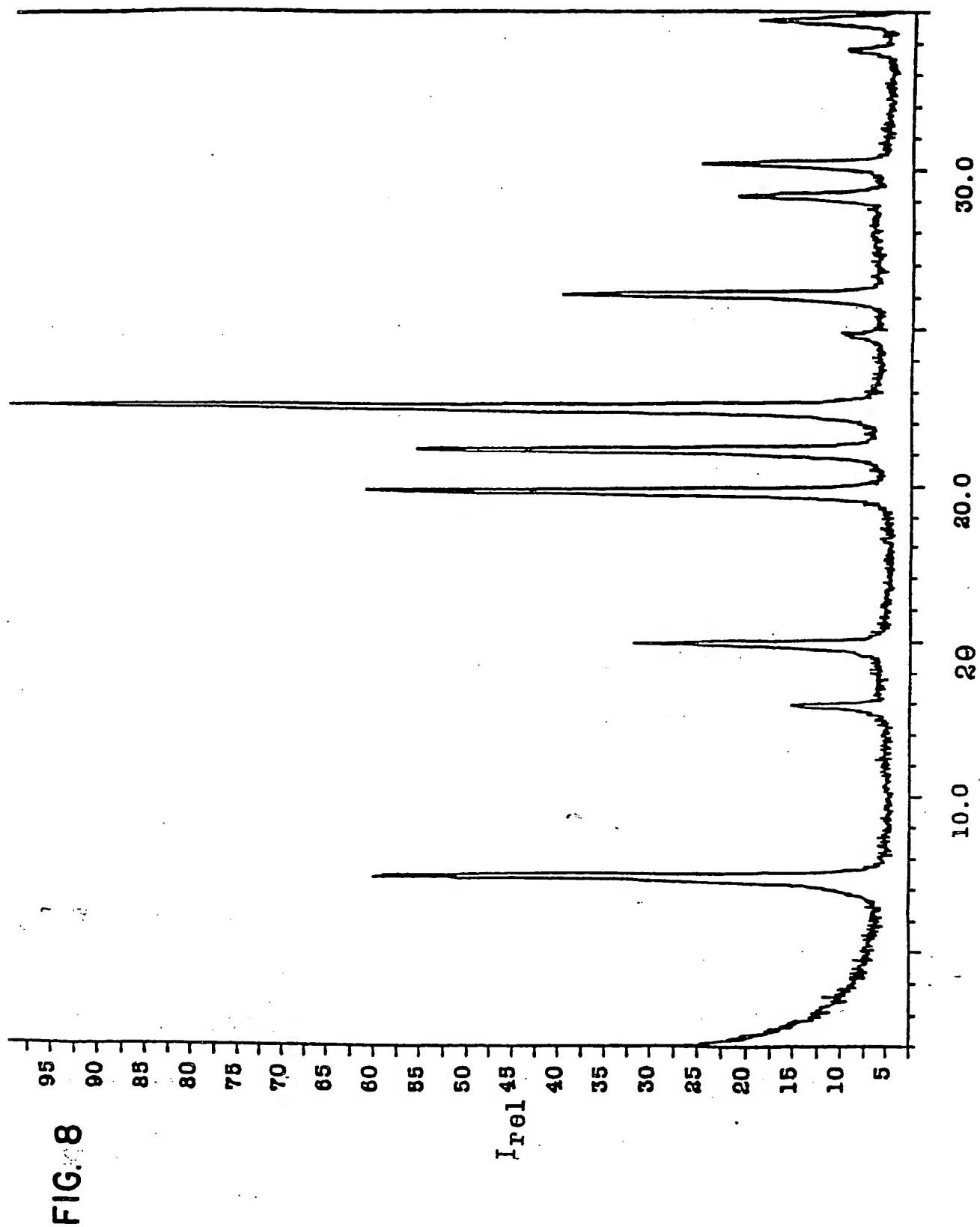


FIG. 7

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# INTERNATIONAL SEARCH REPORT

International Application No PCT/US 89/01366

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (if several classification symbols apply, indicate all) <sup>4</sup> According to International Patent Classification (IPC) or to both National Classification and IPC IPC <sup>4</sup> : C 01 B 25/36, C 01 B 25/45, C 01 B 33/26														
<b>II. FIELDS SEARCHED</b> <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black; margin: 5px 0;">Minimum Documentation Searched <sup>7</sup></div> <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 25%; border-bottom: 1px solid black;">Classification System</th> <th style="border-bottom: 1px solid black;">Classification Symbols</th> </tr> <tr> <td style="border-right: 1px solid black; padding: 5px;">IPC<sup>4</sup></td> <td style="padding: 5px;">C 01 B 25/00, C 01 B 33/00</td> </tr> </table> <div style="border-top: 1px solid black; padding-top: 5px; margin-top: 5px;">           Documentation Searched other than Minimum Documentation            to the Extent that such Documents are Included in the Fields Searched <sup>8</sup> </div>			Classification System	Classification Symbols	IPC <sup>4</sup>	C 01 B 25/00, C 01 B 33/00								
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<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT <sup>9</sup></b> <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 10%; border-bottom: 1px solid black;">Category <sup>*</sup></th> <th style="border-bottom: 1px solid black;">Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup></th> <th style="width: 10%; border-bottom: 1px solid black;">Relevant to Claim No. <sup>13</sup></th> </tr> <tr> <td style="border-right: 1px solid black; text-align: center; vertical-align: top; padding: 5px;">A</td> <td style="padding: 5px;">Nature, vol. 331, no. 6158, 25 February 1988, (London, GB), M.E. Davis et al.: "A molecular sieve with eighteen-membered rings" pages 698-699, see the whole article --</td> <td style="border-right: 1px solid black;"></td> </tr> <tr> <td style="border-right: 1px solid black; text-align: center; vertical-align: top; padding: 5px;">P,A</td> <td style="padding: 5px;">Zeolites, vol. 8, September 1988, (Guildford, GB), M.E. Davis et al.: "VPI-5: The first molecular sieve with pores larger than 10 Ångströms", pages 362-366, see the whole article --</td> <td style="border-right: 1px solid black;"></td> </tr> <tr> <td style="border-right: 1px solid black; text-align: center; vertical-align: top; padding: 5px;">P,A</td> <td style="padding: 5px;">WO, A, 8901912 (THE DOW CHEMICAL CO.) 9 March 1989  -----</td> <td style="border-right: 1px solid black;"></td> </tr> </table> <div style="font-size: small; margin-top: 10px;"> <p><sup>*</sup> Special categories of cited documents: <sup>10</sup></p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&amp;" document member of the same patent family</p> </div>			Category <sup>*</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>	A	Nature, vol. 331, no. 6158, 25 February 1988, (London, GB), M.E. Davis et al.: "A molecular sieve with eighteen-membered rings" pages 698-699, see the whole article --		P,A	Zeolites, vol. 8, September 1988, (Guildford, GB), M.E. Davis et al.: "VPI-5: The first molecular sieve with pores larger than 10 Ångströms", pages 362-366, see the whole article --		P,A	WO, A, 8901912 (THE DOW CHEMICAL CO.) 9 March 1989  -----	
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<b>IV. CERTIFICATION</b> <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%; border-bottom: 1px solid black; padding: 5px;">           Date of the Actual Completion of the International Search            9th August 1989         </td> <td style="width: 50%; border-bottom: 1px solid black; padding: 5px;">           Date of Mailing of this International Search Report  <div style="text-align: right; font-size: large;">21 SEP 1989</div> </td> </tr> <tr> <td style="border-bottom: 1px solid black; padding: 5px;">           International Searching Authority  <div style="text-align: center;">EUROPEAN PATENT OFFICE</div> </td> <td style="border-bottom: 1px solid black; padding: 5px;">           Signature of Authorized Officer  <div style="text-align: right; font-size: large;">T.K. WILLIS</div> </td> </tr> </table>			Date of the Actual Completion of the International Search 9th August 1989	Date of Mailing of this International Search Report <div style="text-align: right; font-size: large;">21 SEP 1989</div>	International Searching Authority <div style="text-align: center;">EUROPEAN PATENT OFFICE</div>	Signature of Authorized Officer <div style="text-align: right; font-size: large;">T.K. WILLIS</div>								
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ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO.

US 8901366  
SA 28321

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 15/09/89  
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO-A- 8901912	09-03-89	AU-A- 2423388	31-03-89

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